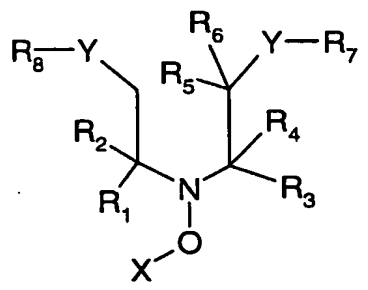
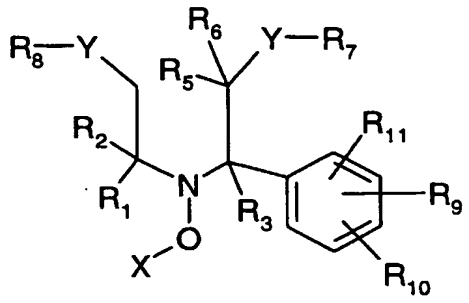
Claims

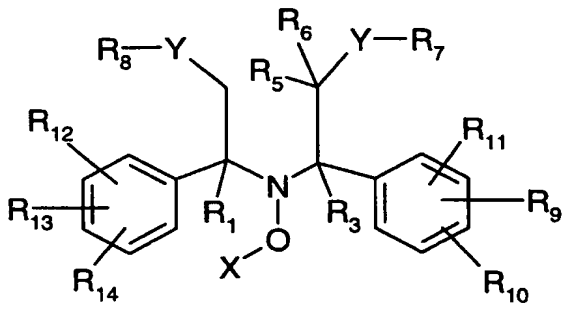
1. A compound of formula Ia, Ib, or Ic



(Ia),



(Ib),



(Ic)

wherein

Y is O or NR_{101} and R_{101} is H or C_1-C_{18}alkyl or R_7 and/or R_8 and R_{101} together with the nitrogen atom to which they are bound form a 5 or 6 membered heterocyclic ring;

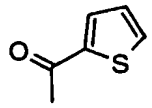
R_1, R_2 and R_3 independently are benzyl, C_1-C_{18}alkyl, C_2-C_{18}alkenyl which are unsubstituted or substituted by OH or by a group –O-C(O)-R_{102}; or C_2-C_{18}alkyl which is interrupted by at least one O atom or a group NR_{102} wherein R_{102} is hydrogen, C_1-C_{18}alkyl or C_6-C_{10}aryl;

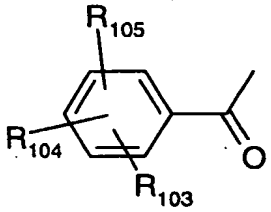
or R_1 and R_2 together with the carbon atom to which they are bound form a C_5-C_{12}cycloalkyl group; or in formula Ia R_3 and R_4 together with the carbon atom to which they are bound form a C_5-C_{12}cycloalkyl group;

R_4 is C_2-C_{12}alkyl;

R_5 and R_6 are independently H, C_1-C_{18}alkyl, C_2-C_{18}alkenyl, benzyl, C_5-C_{12}cycloalkyl or phenyl;

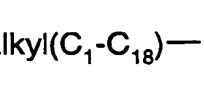
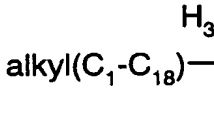
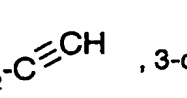
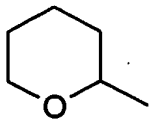
R_7 and R_8 independently are H, C_1-C_{18}alkyl, C_2-C_{18}alkenyl, C_5-C_{12}cycloalkyl or a group

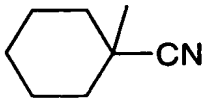
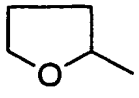
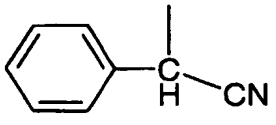
-C(O)-(C_1-C_{18})alkyl, -C(O)-O-(C_1-C_{18})alkyl, -C(O)-O-phenyl, -C(O)-C(O)-OH, -C(O)-C(O)-NH-(C_1-C_{18}alkyl), -C(S)-S-(C_1-C_{18})alkyl,  , -$SiR_aR_bR_c$ wherein R_a , R_b , R_c independently are C_1-C_{18}alkyl or R_7 and R_8 are the following group



wherein R_{103}, R_{104} and R_{105} independently are H, C_1-C_8alkyl, C_1-C_8alkoxy, C_1-C_8alkylthio, -O-C(O)-(C_1-C_8)alkyl, -O-C(O)-(C_6-C_{10})aryl, nitro, cyano or halogen;

R_9, R_{10}, R_{11}, R_{12}, R_{13} and R_{14} independently are H, OH, C_1-C_8alkoxy, C_1-C_8alkyl, SH, C_1-C_8alkylthio,
-O-C(O)-(C_1-C_8)alkyl, -O-C(O)-(C_6-C_{10})aryl, nitro, cyano, halogen or a group $NR_{106}R_{107}$ wherein R_{106} and R_{107} independently are hydrogen, C_1-C_{18}alkyl or C_6-C_{10}aryl or together with the nitrogen atom to which they are bound form a 5 or 6 membered heterocyclic ring; and
X is selected from the group consisting of

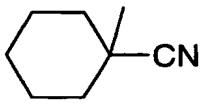
-CH_2-aryl,  , -CH_2-CH_2-aryl,  , (C_5-C_6cycloalkyl)$_2$CCN, (C_1-C_{12}alkyl)$_2$CCN, -$CH_2CH=CH_2$, (C_1-C_{12})alkyl-CR_{20}-C(O)-(C_1-C_{12})alkyl, (C_1-C_{12})alkyl-CR_{20}-C(O)-(C_6-C_{10})aryl, (C_1-C_{12})alkyl-CR_{20}-C(O)-O-R_{21}, (C_1-C_{12})alkyl-CR_{20}-C(O)-phenoxy, (C_1-C_{12})alkyl-CR_{20}-C(O)-N-di(C_1-C_{12})alkyl, (C_1-C_{12})alkyl-CR_{20}-CO-NH(C_1-C_{12})alkyl, (C_1-C_{12})alkyl-CR_{20}-CO-NH_2, -$CH_2CH=CH-CH_3$, -CH_2-$C(CH_3)=CH_2$, -CH_2-CH=CH-phenyl,  , 3-cyclohexenyl, 3-cyclopentenyl,  ,

 ,  and  , wherein

R_{20} is hydrogen or C_1-C_{12}alkyl;

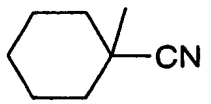
R_{21} is C_1-C_{18}alkyl or C_2-C_{18}alkyl which is interrupted by at least one O atom or a group NR_{102} wherein R_{102} is hydrogen, C_1-C_{18}alkyl or C_6-C_{10}aryl;
the alkyl groups are unsubstituted or substituted with one or more -OH, -COOH, -O(C_1-C_8alkyl), $NR_{106}R_{107}$ or -COR_{20} groups wherein R_{20}, R_{106} and R_{107} have the meanings as defined above;
the aryl groups are phenyl or naphthyl which are unsubstituted or substituted with C_1-C_{12}alkyl, halogen, C_1-C_{12}alkoxy, C_1-C_{12}alkylthio, C_1-C_{12}alkylcarbonyl, glycidyloxy, OH, SH, -COOH or -COO(C_1-C_{12})alkyl.

2. A compound according to claim 1 wherein X is selected from the group consisting of -CH_2-phenyl, CH_3CH-phenyl, $(CH_3)_2C$-phenyl, (C_5-C_6cycloalkyl)$_2$CCN, $(CH_3)_2CCN$,



, -$CH_2CH=CH_2$, CH_3CH-$CH=CH_2$, (C_1-C_8alkyl)CR_{20}-C(O)-phenyl, (C_1-C_8)alkyl-CR_{20}-C(O)-(C_1-C_8)alkoxy, (C_1-C_8)alkyl-CR_{20}-C(O)-(C_1-C_8)alkyl, (C_1-C_8)alkyl-CR_{20}-C(O)-N-di(C_1-C_8)alkyl, (C_1-C_8)alkyl-CR_{20}-C(O)-NH(C_1-C_8)alkyl and (C_1-C_8)alkyl-CR_{20}-C(O)-NH_2, wherein
R_{20} is hydrogen or (C_1-C_8)alkyl.

3. A compound according to claim 2 wherein X is selected from the group consisting of -CH_2-phenyl, CH_3CH-phenyl, $(CH_3)_2C$-phenyl, (C_5-C_6cycloalkyl)$_2$CCN, $(CH_3)_2CCN$,



, -$CH_2CH=CH_2$, CH_3CH-$CH=CH_2$, (C_1-C_4alkyl)CR_{20}-C(O)-phenyl, (C_1-C_4)alkyl-CR_{20}-C(O)-(C_1-C_4)alkoxy, (C_1-C_4)alkyl-CR_{20}-C(O)-(C_1-C_4)alkyl, (C_1-C_4)alkyl-CR_{20}-C(O)-N-di(C_1-C_4)alkyl, (C_1-C_4)alkyl-CR_{20}-C(O)-NH(C_1-C_4)alkyl and (C_1-C_4)alkyl-CR_{20}-C(O)-NH_2, wherein
R_{20} is hydrogen or (C_1-C_4)alkyl.

4. A compound according to claim 1 wherein Y is O and wherein in formula Ia R_4 is C_2-C_6alkyl or R_3 and R_4 together with the carbon atom to which they are bound form a 5 to 7 membered cycloalkyl ring.

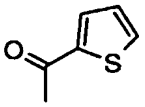
5. A compound according to claim 1 wherein

R_1, R_2 and R_3 are C_1-C_5alkyl; or in formula Ia R_3 and R_4 together with the carbon atom to which they are bound form a C_5-C_6cycloalkyl group;

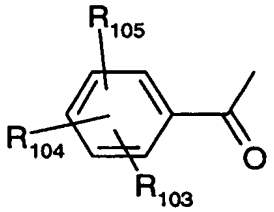
R_4 is C_2-C_6alkyl;

R_5 and R_6 are H;

R_7 and R_8 independently are H, C_1-C_{18}alkyl, allyl, benzyl, C_5-C_{12}cycloalkyl or a group -C(O)-(C_1-C_{18})alkyl, -C(O)-O-(C_1-C_{18})alkyl, -C(O)-C(O)-OH, -C(S)-S-(C_1-C_{18})alkyl,



, -$SiR_aR_bR_c$ wherein R_a , R_b , R_c independently are C_1-C_{18}alkyl or R_7 and R_8 are one of the following groups



wherein R_{103}, R_{104} and R_{105} independently are H, C_1-C_8alkoxy, C_1-C_8alkylthio, -O-C(O)-(C_1-C_8)alkyl, nitro, cyano, halogen, C_1-C_8alkyl;

R_9, R_{10} and R_{11} independently are H, C_1-C_8alkoxy, C_1-C_8alkylthio, -O-C(O)-(C_1-C_8)alkyl, nitro, cyano, halogen or C_1-C_8alkyl; and

X is as defined in claim 1.

6. A compound of formula Ib or Ic according to claim 1.

7. A compound of formula Ib according to claim 1 wherein

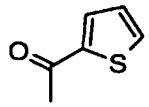
Y is O;

R_1 and R_2 are C_1-C_5alkyl, or together with the carbon atom to which they are bound form a C_5-C_7cycloalkyl group;

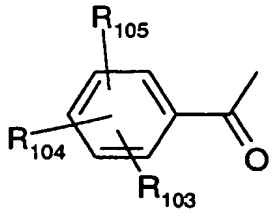
R_3 is methyl, ethyl or propyl;

R_5 and R_6 are H;

R_7 and R_8 independently are H, C_1-C_{18}alkyl, allyl, benzyl, C_5-C_{12}cycloalkyl or a group -C(O)-(C_1-C_{18})alkyl, -C(O)-O-(C_1-C_{18})alkyl, -C(O)-C(O)-OH, -C(S)-S-(C_1-C_{18})alkyl,

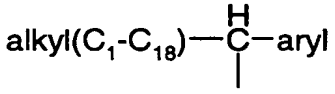
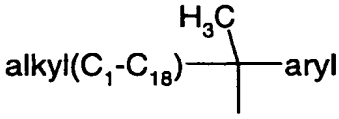
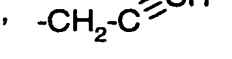
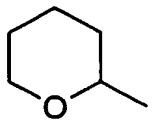
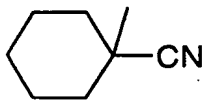
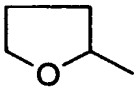
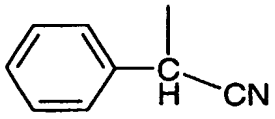


, -$SiR_aR_bR_c$ wherein R_a , R_b , R_c independently are C_1-C_{18}alkyl or R_7 and R_8 are

the following group  wherein R_{103}, R_{104} and R_{105} independently are H, C_1-C_8alkoxy, C_1-C_8alkylthio, -O-C(O)-(C_1-C_8)alkyl, nitro, cyano, halogen, C_1-C_8alkyl;

R_9, R_{10} and R_{11} independently are H, C_1-C_8alkoxy, C_1-C_8alkylthio, -O-C(O)-(C_1-C_8)alkyl, nitro, cyano, halogen or C_1-C_8alkyl; and

X is selected from the group consisting of

-CH_2-aryl,  , -CH_2-CH_2-aryl,  , (C_5-C_6cycloalkyl)$_2$CCN, (C_1-C_{12}alkyl)$_2$CCN, -$CH_2CH=CH_2$, (C_1-C_{12})alkyl-CR_{20}-C(O)-(C_1-C_{12})alkyl, (C_1-C_{12})alkyl-CR_{20}-C(O)-(C_6-C_{10})aryl, (C_1-C_{12})alkyl-CR_{20}-C(O)-O-R_{21}, (C_1-C_{12})alkyl-CR_{20}-C(O)-phenoxy, (C_1-C_{12})alkyl-CR_{20}-C(O)-N-di(C_1-C_{12})alkyl, (C_1-C_{12})alkyl-CR_{20}-CO-NH(C_1-C_{12})alkyl, (C_1-C_{12})alkyl-CR_{20}-CO-NH_2, -$CH_2CH=CH-CH_3$, -CH_2-$C(CH_3)=CH_2$, -CH_2-CH=CH-phenyl,  , 3-cyclohexenyl, 3-cyclopentenyl,  ,  ,  or  , wherein

R_{20} is hydrogen or C_1-C_{12}alkyl;

R_{21} is C_1-C_{18}alkyl or C_2-C_{18}alkyl which is interrupted by at least one O atom or a group NR_{102} wherein R_{102} is hydrogen, C_1-C_{18}alkyl or C_6-C_{10}aryl;

the alkyl groups are unsubstituted or substituted with one or more -OH, -COOH, -O(C_1-C_8alkyl), $NR_{106}R_{107}$ or -COR_{20} groups wherein R_{20}, R_{106} and R_{107} have the meanings as defined above;

the aryl groups are phenyl or naphthyl which are unsubstituted or substituted with C_1-C_{12}alkyl, halogen, C_1-C_{12}alkoxy, C_1-C_{12}alkylcarbonyl, glycidyloxy, OH, -COOH or -COO(C_1-C_{12})alkyl.

8. A polymerizable composition, comprising
a) at least one ethylenically unsaturated monomer or oligomer, and
b) a compound according to formula (Ia) (Ib) or (Ic) according to claim 1.

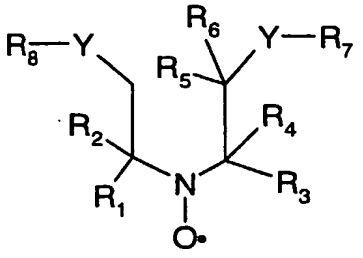
9. A process for preparing an oligomer, a cooligomer, a polymer or a copolymer (block or random) by free radical polymerization of at least one ethylenically unsaturated monomer or oligomer, which comprises (co)polymerizing the monomer or monomers/oligomers in the presence of an initiator compound of formula (Ia), (Ib) or (Ic) according to claim 1 under reaction conditions capable of effecting scission of the O-X bond to form two free radicals, the radical •X being capable of initiating polymerization.

10. A process according to claim 9 wherein the scission of the O-X bond is effected by ultrasonic treatment, heating or exposure to electromagnetic radiation, ranging from γ to microwaves.

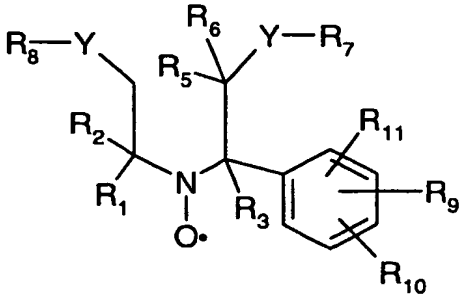
11. A process according to claim 10 wherein the scission of the O-X bond is effected by heating and takes place at a temperature of between 50°C and 160°C.

12. A process according to claim 9 wherein the compound is present in an amount from 0.001 mol-% to 20 mol-% , based on the monomer or monomer mixture.

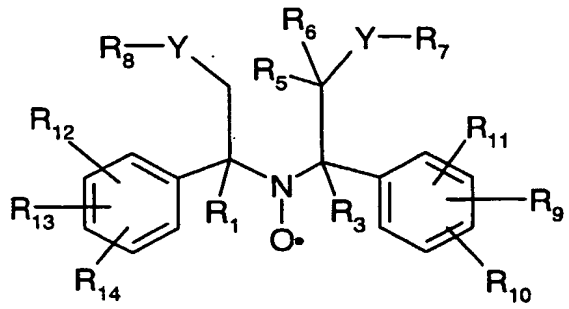
13. A polymerizable composition, comprising
a) at least one ethylenically unsaturated monomer or oligomer, and
b) a compound according to formula (IIa) (IIb) or (IIc)



(IIa),



(IIb) ,



(IIc)

wherein

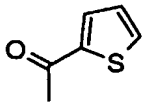
Y is O or NR_{101} and R_{101} is H or C_1-C_{18}alkyl or R_7 and/or R_8 and R_{101} together with the nitrogen atom to which they are bound form a 5 or 6 membered heterocyclic ring;

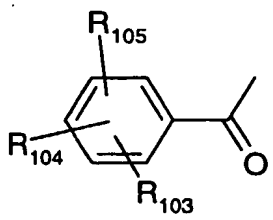
R_1, R_2 and R_3 independently are benzyl, C_1-C_{18}alkyl, C_2-C_{18}alkenyl which are unsubstituted or substituted by OH or a by group –O-C(O)-R_{102}; or C_2-C_{18}alkyl which is interrupted by at least one O atom or a group NR_{102} wherein R_{102} is hydrogen, C_1-C_{18}alkyl or C_6-C_{10}aryl;

or R_1 and R_2 together with the carbon atom to which they are bound form a C_5-C_{12}cycloalkyl group; or in formula Ia R_3 and R_4 together with the carbon atom to which they are bound form a C_5-C_{12}cycloalkyl group;

R_4 is C_2-C_{12}alkyl;

R_5 and R_6 are independently H, C_1-C_{18}alkyl, C_2-C_{18}alkenyl, benzyl, C_5-C_{12}cycloalkyl or phenyl;

R_7 and R_8 independently are H, C_1-C_{18}alkyl, C_2-C_{18}alkenyl, C_5-C_{12}cycloalkyl or a group -C(O)-(C_1-C_{18})alkyl, -C(O)-O-(C_1-C_{18})alkyl, -C(O)-O-phenyl, -C(O)-C(O)-OH, -C(O)-C(O)-NH-(C_1-C_{18}alkyl), -C(S)-S-(C_1-C_{18})alkyl,  , -$SiR_aR_bR_c$ wherein R_a, R_b, R_c independently are C_1-C_{18}alkyl or R_7 and R_8 are the following group



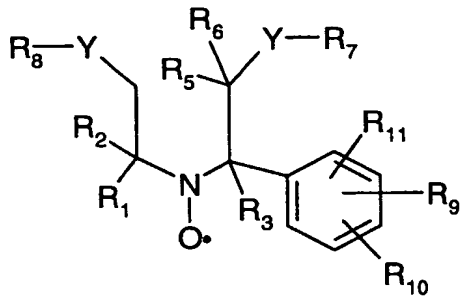
wherein R_{103}, R_{104} and R_{105} independently are H, C_1-C_8alkyl, C_1-C_8alkoxy, C_1-C_8alkylthio, -O-C(O)-(C_1-C_8)alkyl, -O-C(O)-(C_6-C_{10})aryl, nitro, cyano or halogen;

R_9, R_{10}, R_{11}, R_{12}, R_{13} and R_{14} independently are H, OH, C_1-C_8alkoxy, C_1-C_8alkyl, SH, C_1-C_8alkylthio,

-O-C(O)-(C_1-C_8)alkyl, -O-C(O)-(C_6-C_{10})aryl, nitro, cyano, halogen or a group $NR_{106}R_{107}$ wherein R_{106} and R_{107} independently are hydrogen, C_1-C_{18}alkyl or C_6-C_{10}aryl or together with the nitrogen atom to which they are bound form a 5 or 6 membered heterocyclic ring;
and
c) a source of free radicals capable of initiating polymerization of ethylenically unsaturated monomers.

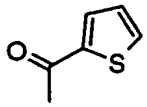
14. A process for preparing an oligomer, a cooligomer, a polymer or a copolymer (block or random) by free radical polymerization of at least one ethylenically unsaturated monomer/oligomer, which comprises subjecting the composition according to claim 13 to heat or actinic radiation.

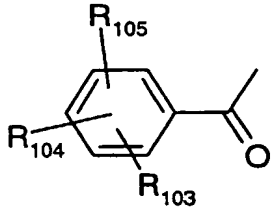
15. A compound of formula IIb



(IIb) ,

wherein
Y is O or NR_{101} and R_{101} is H or C_1-C_{18}alkyl or R_7 and R_{101} together with the nitrogen atom to which they are bound form a 5 or 6 membered heterocyclic ring;
R_1, R_2 and R_3 independently are benzyl, C_1-C_{18}alkyl, C_2-C_{18}alkenyl which are unsubstituted or substituted by OH or a group –O-C(O)-R_{102}; or C_2-C_{18}alkyl which is interrupted by at least one O atom or a group NR_{102} wherein R_{102} is hydrogen, C_1-C_{18}alkyl or C_6-C_{10}aryl;
or R_1 and R_2 together with the carbon atom to which they are bound form a C_5-C_{12}cycloalkyl group;
R_5 and R_6 are independently H, C_1-C_{18}alkyl, C_2-C_{18}alkenyl, benzyl, C_5-C_{12}cycloalkyl or phenyl;
R_7 and R_8 independently are H, C_1-C_{18}alkyl, C_2-C_{18}alkenyl, C_5-C_{12}cycloalkyl or a group

-C(O)-(C_1-C_{18})alkyl, -C(O)-O-(C_1-C_{18})alkyl, -C(O)-O-phenyl, -C(O)-C(O)-OH, -C(O)-C(O)-NH-(C_1-C_{18}alkyl), -C(S)-S-(C_1-C_{18})alkyl,  , -$SiR_aR_bR_c$ wherein R_a , R_b , R_c independently are C_1-C_{18}alkyl or R_7 and R_8 are one of the following groups



wherein R_{103}, R_{104} and R_{105} independently are H, C_1-C_8alkyl, C_1-C_8alkoxy, C_1-C_8alkylthio, -O-C(O)-(C_1-C_8)alkyl, -O-C(O)-(C_6-C_{10})aryl, nitro, cyano or halogen;

R_9, R_{10} and R_{11} independently are H, OH, C_1-C_8alkoxy, C_1-C_8alkyl, SH, C_1-C_8alkylthio, -O-C(O)-(C_1-C_8)alkyl, -O-C(O)-(C_6-C_{10})aryl, nitro, cyano, halogen or a group $NR_{106}R_{107}$ wherein R_{106} and R_{107} independently are hydrogen, C_1-C_{18}alkyl or C_6-C_{10}aryl or together with the nitrogen atom to which they are bound form a 5 or 6 membered heterocyclic ring.

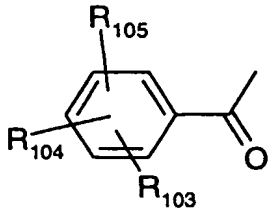
16. A compound of formula IIb according to claim 15 wherein

Y is O;

R_1 and R_2 are $-CH_3$, or together with the carbon atom to which they are bound form a C_5-C_7cycloalkyl group;

R_3 is methyl, ethyl or propyl;

R_5 and R_6 are H;

R_7 and R_8 independently are H, C_1-C_{18}alkyl, allyl, benzyl, C_5-C_{12}cycloalkyl or a group -C(O)-(C_1-C_{18})alkyl, -C(O)-O-(C_1-C_{18})alkyl, -C(O)-C(O)-OH, -C(S)-S-(C_1-C_{18})alkyl, -$SiR_aR_bR_c$ wherein R_a , R_b , R_c independently are C_1-C_{18}alkyl or R_7 and R_8 are one of the following groups  wherein R_{103}, R_{104} and R_{105} independently are H, C_1-C_8alkoxy, C_1-C_8alkylthio, -O-C(O)-(C_1-C_8)alkyl, nitro, cyano, halogen, C_1-C_8alkyl;

and

R_9, R_{10} and R_{11} independently are H, C_1-C_8alkoxy, C_1-C_8alkylthio, -O-C(O)-(C_1-C_8)alkyl, nitro, cyano, halogen or C_1-C_8alkyl.

17. Use of a compound of formula Ia, Ib or Ic according to claim 1 for the polymerization of ethylenically unsaturated monomers.

18. Use of a compound of formula IIa, IIb or IIc according to claim 13 together with a source of free radicals for the polymerization of ethylenically unsaturated monomers.

19. A polymer or copolymer obtainable by a process according to claim 9 or 14.